Atmospheric Pressure Ionization Mass Spectrometry Techniques for the Analysis of Alkyl Ethoxysulfate Mixtures

Brent N. Jewett, Louis Ramaley, and Jan C. T. Kwak
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada

This paper compares two liquid introduction atmospheric pressure ionization techniques for the analysis of alkyl ethoxysulfate (AES) anionic surfactant mixtures by mass spectrometry, i.e., electrospray ionization (ESI) in both positive and negative ion modes and atmospheric pressure chemical ionization (APCI) in positive ion mode, using a triple quadrupole mass spectrometer. Two ions are observed in ESI(+) for each individual AES component, $[M + Na]^+$ and a "desulfated" ion $[M - SO_3 + H]^+$, whereas only one ion, $[M - Na]^-$ is observed for each AES component in ESI(−). APCI(+) produces a protonated, "desulfated" ion of the form $[M - NaSO_3 + 2H]^+$ for each AES species in the mixture under low cone voltage (10 V) conditions. The mass spectral ion intensities of the individual AES components in either the series from ESI(+) or APCI(+) can be used to obtain an estimate of their relative concentrations in the mixture and of the average ethoxylate (EO) number of the sample. The precursor ions produced by either ESI(+) or ESI(−), when subjected to low-energy (50 eV) collision-induced dissociation, do not fragment to give ions that provide much structural information. The protonated, desulfated ions produced by APCI(+) form fragment ions which reveal structural information about the precursor ions, including alkyl chain length and EO number, under similar conditions. APCI(+) is less susceptible to matrix effects for quantitative work than ESI(+). Thus APCI(+) provides an additional tool for the analysis of anionic surfactants such as AES, especially in complex mixtures where tandem mass spectrometry is required for the identification of the individual components. (J Am Soc Mass Spectrom 1999, 10, 529–536) © 1999 American Society for Mass Spectrometry

Anionic surfactants comprise approximately 65% of the worldwide production of surfactants [1]. Their main applications include use as soaps, detergents, and emulsifiers [2]. Commercial surfactants are most often mixtures with compositions governed by starting material economics and formulation considerations. Alkyl ethoxysulfates (AES), whose general structural form is $CH_3(CH_2)_x(OCH_2CH_2)_nOSO_3^-Z^+$ (where Z is the counterion), are a small but rapidly growing class of anionic surfactants found in many commercial products. By the nature of their synthesis and/or formulation, these surfactants contain a mixture of individual species having a range of ethoxylate oligomers and, often, a mixture of alkyl chain lengths as well. In certain instances, it is desirable to know what specific components are in the mixture and in what quantity. For example, the growing interest in the fate of surfactants in the aquatic environment has created a demand for methods for the analysis of individual surfactants in complex matrices because surfactant biodegradability is dependent upon both alkyl chain length and, in the case of AES, the number of ethoxylate groups in the molecule [3]. For samples that have not been subjected to a prior separation procedure, the presence of a large number of peaks, some of which may be unresolved multiplets, in the mass spectrum remains a challenge in the analysis of these important compounds.

For the AES mixture investigated, Dobanol 23PES04, the counterion was Na^+. Dobanol, also known in the U.S. as Neodol, is a registered trademark of the Shell Development Company for the linear alcohol mixtures used as starting materials for the synthesis of the alkyl ethoxysulfates. The digits "23" indicate a C_{12} and C_{13} alkyl chain mixture; "PES" stands for (propoxy/ethoxy) sulfate and the last two digits represent the average number of propylene oxide (PO) groups and ethylene oxide (EO) groups in the molecules, respectively. The first digit will always be zero for the alkyl ethoxysulfates.

Mass spectrometry (MS) offers the advantages of high sensitivity, selectivity, and relative simplicity in the analysis of mixtures such as AES. The advent of liquid introduction ionization techniques such as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) [4] makes mass spectrometry even more applicable for such analyses because it

Address reprint requests to Jan C. T. Kwak, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada. E-mail: jkwak@chem1.chem.dal.ca

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removes the need to extract the analyte from solution and permits the coupling of high performance liquid chromatography (HPLC) with mass spectrometry [5]. Furthermore, tandem mass spectrometry (MS/MS) [6] can be used to identify and/or obtain structural information on a particular component of interest. To our knowledge, very little work on sulfated anionic surfactants using atmospheric pressure ionization techniques has appeared in the literature [7, 8]. In fact, we are aware of only one publication describing the analysis of AES by ESI (in negative ion mode) [7]. In this article, the emphasis is placed on the quantitative analysis of individual AES species in environmental matrices. Earlier work on AES using fast-atom bombardment (FAB) as the ionization technique used neat AES mixtures as opposed to AES mixtures in solution [9].

ESI is perhaps the most obvious ionization method for the analysis of the AES anionic surfactants because it provides good results for analytes that are already "preionized" in solution. Both ESI(+) and ESI(−) readily produce ions for individual AES components. APCI may not seem to be as good a choice for the analysis of anionic surfactants such as AES. However, our results indicate that APCI(+) also produces ions which are useful in both a qualitative and quantitative sense. In this paper, we will demonstrate that APCI is an effective tool for the analysis of AES surfactants in solution, and we will compare the results of both ESI and APCI liquid introduction methods for the analysis of a commercial AES surfactant mixture containing a range of alkyl groups and EO oligomers.

Experimental

The alkyl ethoxysulfate mixture studied, Dobanol 23PES04 (62.7% active matter content in water), was obtained from Shell Laboratories, Amsterdam, The Netherlands. The pure alcohol ethoxylate used in the spiking experiment [$C_{12}H_{25}(OCH_2CH_2)_6OH$] was obtained from TCI America (Portland OR) and was reported as 99% pure. All mass spectral data were acquired using a Fisons VG Quattro (I) triple quadrupole mass spectrometer with a Quattro (II) ESI/APCI interface. Data acquisition and data processing were done using MassLynx V2.1 software. In ESI mode, solvent was delivered by a 10 mL Hamilton Gas-Tight syringe (#1010) mounted on a Cole-Palmer Instrument (Model 74900) syringe pump. A Shimadzu LC-10 AT liquid chromatograph pump was used to deliver solvent(s) in APCI mode. In both cases a Rheodyne 6-port injector (Model 7125) was used for sample injections. All solvents (methanol, acetonitrile, and acetone) were HPLC grade obtained from Aldrich Chemical (Milwaukee, WI). All water was deionized and purified in-house using a Millipore R/Q water purification system. Glacial acetic acid (99.7%, British Drug House, Poole, England) and ammonium acetate (reagent grade, Mallinkrodt, St. Louis, MO) were used as mobile phase additives. Polyethylene glycols (PEG) 200, 400, 800, and 1000, used in the calibration solution, were obtained from Aldrich Chemical. All nitrogen used in the operation of the ESI and APCI interfaces was produced in-house via liquefaction of air.

Calibration of the mass spectrometer was done in ESI(+) mode using a solution comprised of 250 ppm of PEG 200, 500 ppm of PEG 400, 750 ppm of PEG 800, and 2500 ppm of PEG 1000 in 1:1 (v/v) acetonitrile:0.002 M ammonium acetate (aq). Ammoniated molecular ions were formed over the entire mass range between *m/z* 50 and 1200. Calibration was deemed successful when MS1 and MS2 were calibrated to within ±0.1 Da.

High-purity grade argon (Liquid Carbonic, Scarborough, ON) was used as the collision gas for MS/MS experiments. The collision gas pressure was adjusted until the intensity of the precursor ion in the second mass analyzer decreased by 50%. The collision energy was set at 50 eV for all spectra acquired in ESI mode and 40 eV in APCI mode.

Results and Discussion

Structural Information

The ESI(+) and APCI(+) mass spectra for Dobanol 23PES04 are given in Figure 1. ESI(+) produced two overlapping series of ions: an $[M_1 + Na]^+$ series representing each alkyl ethoxysulfate in the mixture where M_1 is the ion pair $R(OCH_2CH_2)_nOSO_3^-Na^+$ and an $[M_2 + Na]^+$ ion series for the corresponding "unsulfated" alcohol ethoxylates where M_2 is $R(OCH_2CH_2)_nOH$ [Figure 1(a)]. The ESI(+) mass spectrum in Figure 1a can be viewed as repeating units of three ions which account for the two ion series. The lowest mass ion in each repeating unit or triad originates from the alcohol ethoxylate series and has the structural form $[C_{12}H_{25}(OCH_2CH_2)_{n+2}OH + Na]^+$, the highest mass ion in the triad originates from the alkyl ethoxysulfate ion series and has the structural form $[C_{13}H_{27}(OCH_2CH_2)_nOSO_3^-Na^+ + Na]^+$ whereas the central peak is a mixture of two ions, one from each of the two ion series, i.e., $[C_{13}H_{27}(OCH_2CH_2)_{n+2}OH + Na]^+$ and $[C_{12}H_{25}(OCH_2CH_2)_nOSO_3^-Na^+ + Na]^+$. Thus, singlet ions are only observed for alkyl ethoxysulfates with C_{13} alkyl chains and for alcohol ethoxylates with C_{12} alkyl chains.

One reviewer has suggested the use of other alkali metal ions, e.g., K^+, as counterion (and thus attachment ion) to remove this overlap. There are several reasons why this was not done. (1) The counterion associated with AES will be Na^+ in almost all cases for real samples. Thus changing counterions would involve a time consuming ion exchange step with the possibility of adding error and reducing sensitivity. (2) Sodium is the only common alkali metal that is monoisotopic. Substitution of another alkali metal will complicate the observed spectra. (3) Substitution of potassium in particular does not remove the overlap problem, it only changes it. For K^+ as counterion, the ions $[C_{12}H_{25}(EO)_{n+3}OH + K]^+$ and $[C_{13}H_{27}(EO)_nSO_4^-K^+ +$

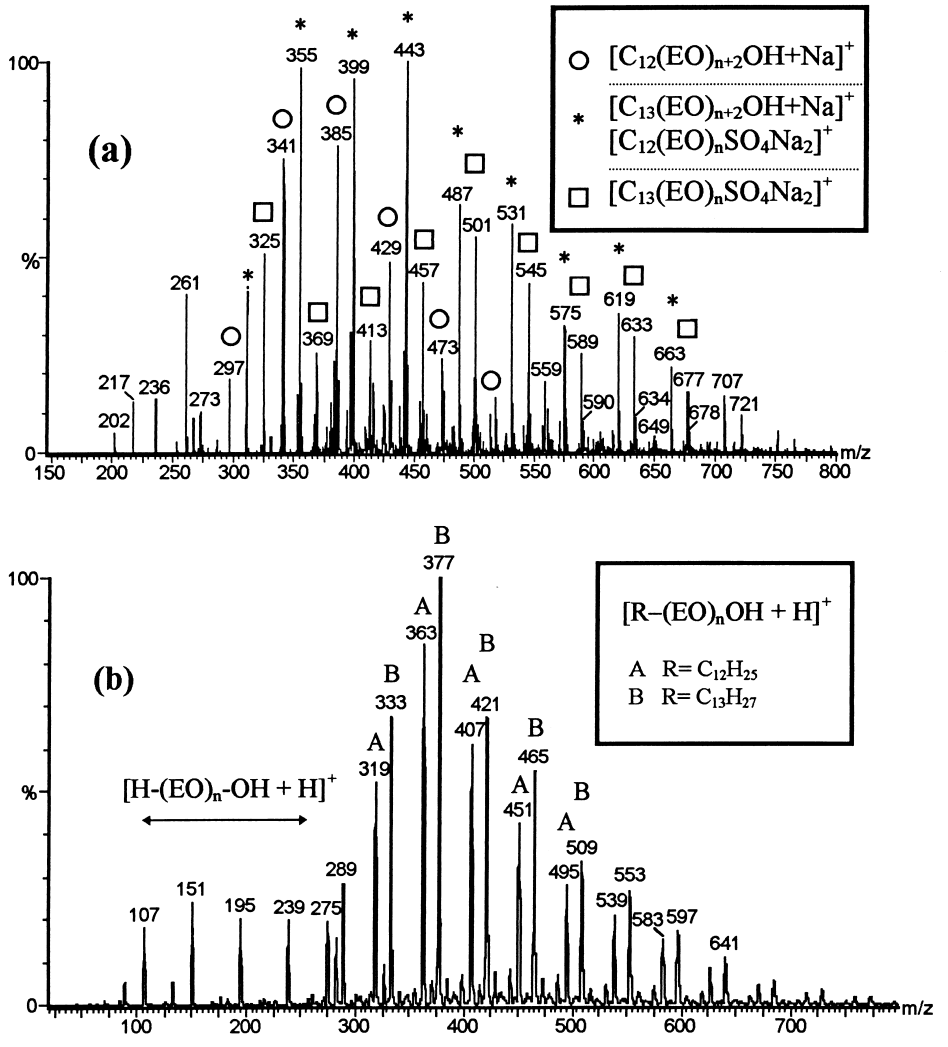

Figure 1. **(a)** ESI(+) mass spectrum of Dobanol 23PES04 (1000 ppm in 1:1 MeOH:H_2O (v/v), 10 μL injection into a 20 μL/min flow of 1:1 MeOH:H_2O with 1% CH_3COOH, source temperature −80 °C, cone −30 V). **(b)** APCI(+) mass spectrum of Dobanol 23PES04 (1000 ppm in 1:1 MeOH:H_2O (v/v), 10 μL injection into a 200 μL/min flow of 1:1 MeOH:H_2O with 1% CH_3COOH, source temperature −120 °C, probe temperature −500 °C, cone −30 V).

$K]^+$ have the same mass. Singlet ions would only be observed for alcohol ethoxylates with C_{13} alkyl chains and alkyl ethoxysulfates with C_{12} alkyl chains in this case.

The presence of the alcohol ethoxylate ion series may be due to the presence of unreacted starting material (see below), because alcohol ethoxylates are the precursors used in the synthesis of alkyl ethoxysulfates [1]. It is also possible that the observed alcohol ethoxylate ion series may be due to hydrolysis of the sulfate group from alkyl ethoxysulfates over the course of long-term shelf storage. However, the possibility that the alcohol ethoxylate ion series is somehow due to loss of SO_3, which for simplicity will be referred to as "desulfation," from the alkyl ethoxysulfates in the ion source (i.e., the possibility that there are two ion series for each alkyl ethoxysulfate) is less likely given that ESI, by its very nature, is a very "soft" ionization technique.

To obtain an estimate of the free alcohol content of the analysis mixture and of the relative sensitivities of the $[M_1 + Na]^+$ ions of the alkyl ethoxysulfates versus the $[M_2 + Na]^+$ ions of the alcohol ethoxylates (i.e., to approximate the ratio of sulfate to free alcohol), a standard addition experiment was performed. Known amounts of pure alcohol ethoxylate, $C_{12}H_{25}(OCH_2CH_2)_6OH$, were added to a constant amount of Dobanol 23PES04. The ion intensity of the *m/z* 473 peak (corresponding to $[C_{12}H_{25}(OCH_2CH_2)_6OH + Na]^+$) was then monitored as a function of the amount of alcohol ethoxylate added. Ion currents for the *m/z* 473 ion are reported in Table 1.

From the standard addition experiment for the unsulfated alcohol ethoxylate, which shows only small deviations from linearity in the ion current at these concentrations, and assuming no fragmentation, we find that the $C_{12}(EO)_6OH$ content in 500 μg of surfactant is not higher than 1.2 ± 0.3 μg. From the ion currents

Table 1. Standard addition experiment for the *m/z* = 473 ion, $[C_{12}H_{25}(EO)_6OH + Na]^+$, in ESI(+) mode

Dobanol 23PES04 injected (μg)	$C_{12}H_{25}(EO)_6OH$ added (μg)	*m/z* 473 ion intensity
492	0	61,600
496	0.6	113,000
504	1.4	137,000
518	5.1	280,000
522	10.8	483,000

for the C_{12} alcohol ethoxylates in Figure 1a, assuming a linear response in moles of compound, we estimate that the total mass of these compounds in 500 μg of surfactant is approximately 13 μg. Using data for Dobanol 23S (not shown), the unethoxylated sulfate which is derived from the same hydrocarbon feedstock as the ethoxylated sulfates and which gives a C_{12}/C_{13} ratio of 0.78, we estimate that the C_{13} alcohol ethoxylates comprise 17 μg out of 500 μg of the same Dobanol 23PES04 sample. Independently, a value of 16 μg is obtained from the ion currents remaining after the ion currents of the corrected C_{13} alkyl ethoxysulfate peaks are subtracted from the unresolved C_{13} alcohol ethoxylate and C_{12} alkyl ethoxysulfate peaks, indicating that the data are internally consistent. Thus at most 30 μg, or 6%, of the 500 μg sample is unsulfated alcohol. This experiment indicates that ESI(+) is considerably more sensitive to the alcohol than to the sulfate, and that the unsulfated alcohol content in the commercial sample is relatively small.

Low-energy CID spectra of one of the singlet ions in both series are given in Figure 2. Figure 2a is the 50 eV ESI(+) MS/MS spectrum of an ion in the alkyl ethoxysulfate, $[M_1 + Na]^+$, series at *m/z* 413 corresponding to $[C_{13}H_{27}(OCH_2CH_2)_2OSO_3^-Na^+ + Na]^+$. Two product ions are formed corresponding to Na^+ (*m/z* 23) and $Na_2HSO_4^+$ (*m/z* 143). However, no product ions are observed which provide useful information on the ethylene oxide content or alkyl chain length in the precursor ion (i.e., ions formed as the result of ether cleavages). Similarly, Figure 2b represents the 50 eV ESI(+) MS/MS spectrum for an ion in the alcohol ethoxylate, $[M_2 + Na]^+$, series at *m/z* 385, corresponding to $[C_{12}H_{25}(OCH_2CH_2)_4OH + Na]^+$. The only product ion formed is the Na^+ ion at *m/z* 23, which again reveals no structural information. These data agree with earlier observations made by Lattimer and co-workers on similar polyglycols using FAB [10, 11].

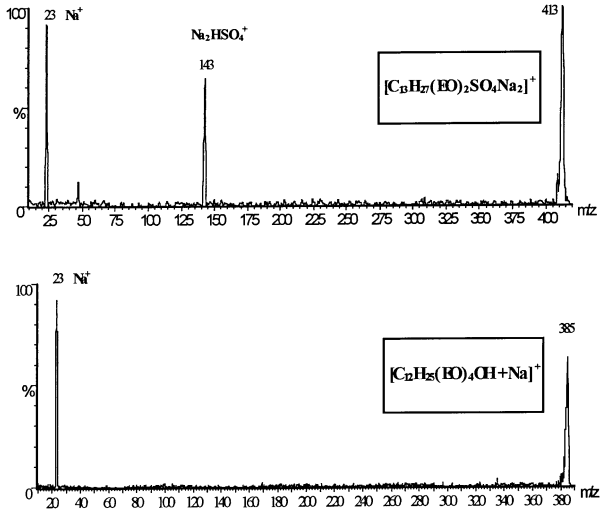

Figure 2. ESI(+) MS/MS spectra of the *m/z* 385 and *m/z* 413 ions in Dobanol 23PES04 (CID gas–argon, collision energy −50 eV, analyzer pressure -3.0×10^{-5} mbar).

Lattimer et al. found that replacement of the sodium counterion (and, as a result, the attachment ion) with lithium improved the production of structurally informative product ions in the MS/MS spectra of polyglycols [11, 12]. This observation was attributed to the fact that the lithium atom was more tightly bound to the oxygen atom(s) in polyglycols than was sodium, which meant that all of the CID energy was not channeled into the production of the alkali metal cation itself, but rather other, more structurally informative product ions.

To explore this possibility, lithiation of Dobanol 23PES04 was performed using cation exchange. The lithiated sample was then subjected to ESI(+) ionization. The major ion series produced was of the form $[M_3 + Li]^+$ [where M_3 is $R(OCH_2CH_2)_nOSO_3^-Li^+$]. A particular ion from this series was selected and subjected to low energy CID. An example of the MS/MS spectrum for the ion at *m/z* 499 (corresponding to $[C_{12}H_{25}(OCH_2CH_2)_5OSO_3^-Li^+ + Li]^+$) is given in Figure 3. The favored product ions correspond to the loss of SO_3 and $LiHSO_4$ from the molecular ion, respectively. The ion at *m/z* 375 is indicative of the loss of an EO group from the ion at *m/z* 419, but no further information on the precursor ion was obtained. It is obvious that the ease of the loss of sulfate (as SO_3 and $LiHSO_4$) is the main reason we do not observe more structurally informative product ions in the low energy CID spectrum.

ESI(−) of the alkyl ethoxysulfates produced ions of the form $[M_1 - Na]^-$, which, under low energy CID conditions, gave product ions at *m/z* 97 ($[HSO_4]^-$) and *m/z* 80 ($[SO_3]^{-\cdot}$). An example of this, for $[C_{13}H_{27}(EO)_4SO_4]^-$, is shown in Figure 4. Again, little, if any, structural information was obtained. A tiny amount of the product ion at *m/z* 123 (corresponding to $[CH_2{=}CH{-}OSO_3]^-$) indicates that ethylene oxide is present in the precursor ion, but this was the only ion observed regardless of the number of EO units in the precursor ion. As expected, the presence of an $[M_2 - H]^-$ ion series for the alcohol ethoxylate was not observed in ESI(−) mode. A separate spiking experiment with pure alcohol ethoxylate showed that ESI(−) did not produce $[M_2 - H]^-$ ions under our experimental conditions, even at high concentrations.

The APCI(+) mass spectrum of Dobanol 23PES04 is given in Figure 1b. Only one ion series was observed of

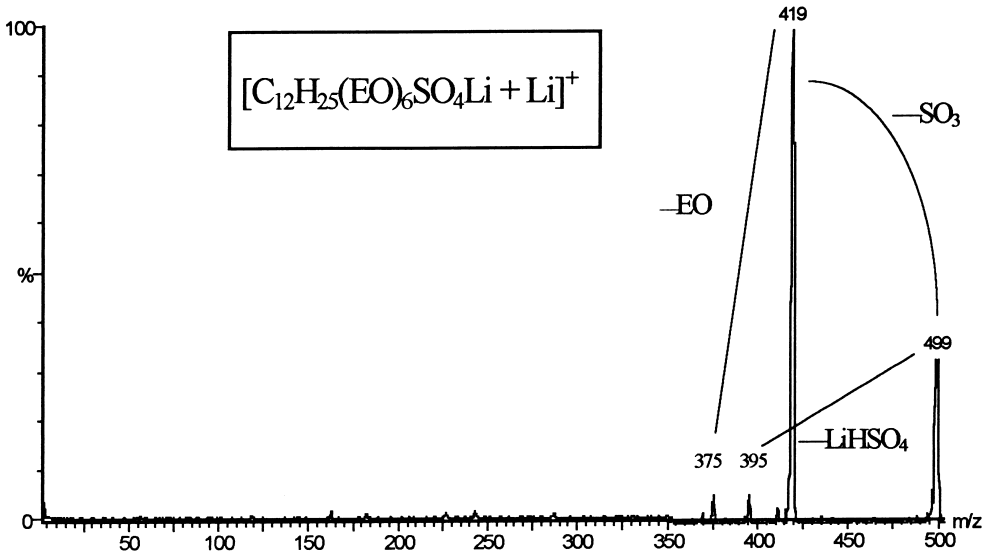

Figure 3. ESI(+) MS/MS spectrum of the $[C_{12}H_{25}(EO)_6SO_4^-Li^+ + Li]^+$ ion (*m/z* 499) in lithiated Dobanol 23PES04 (CID gas–argon, collision energy −50 eV, analyzer pressure -3.0×10^{-5} mbar).

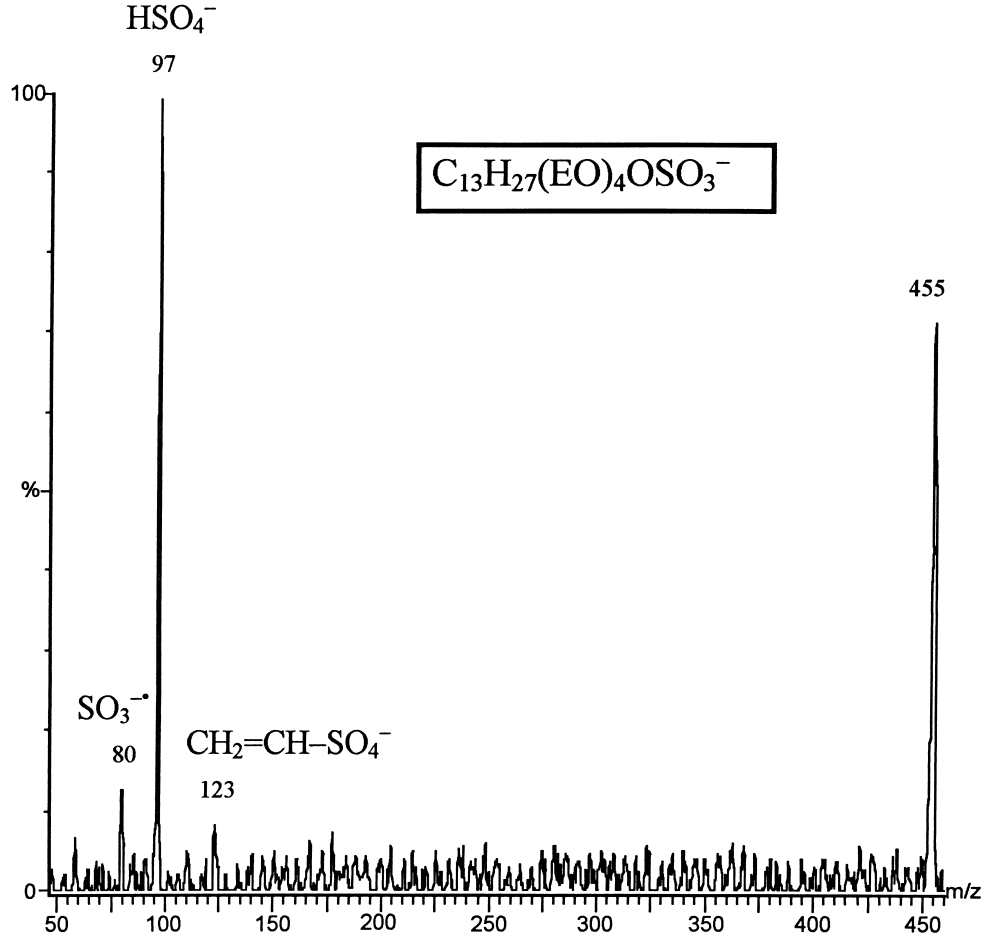

Figure 4. ESI(−) MS/MS spectrum of the $[C_{13}H_{27}(EO)_4SO_4]^-$ ion (*m/z* 455) in Dobanol 23PES04 (CID gas–argon, collision energy −50 eV, analyzer pressure -3.0×10^{-5} mbar).

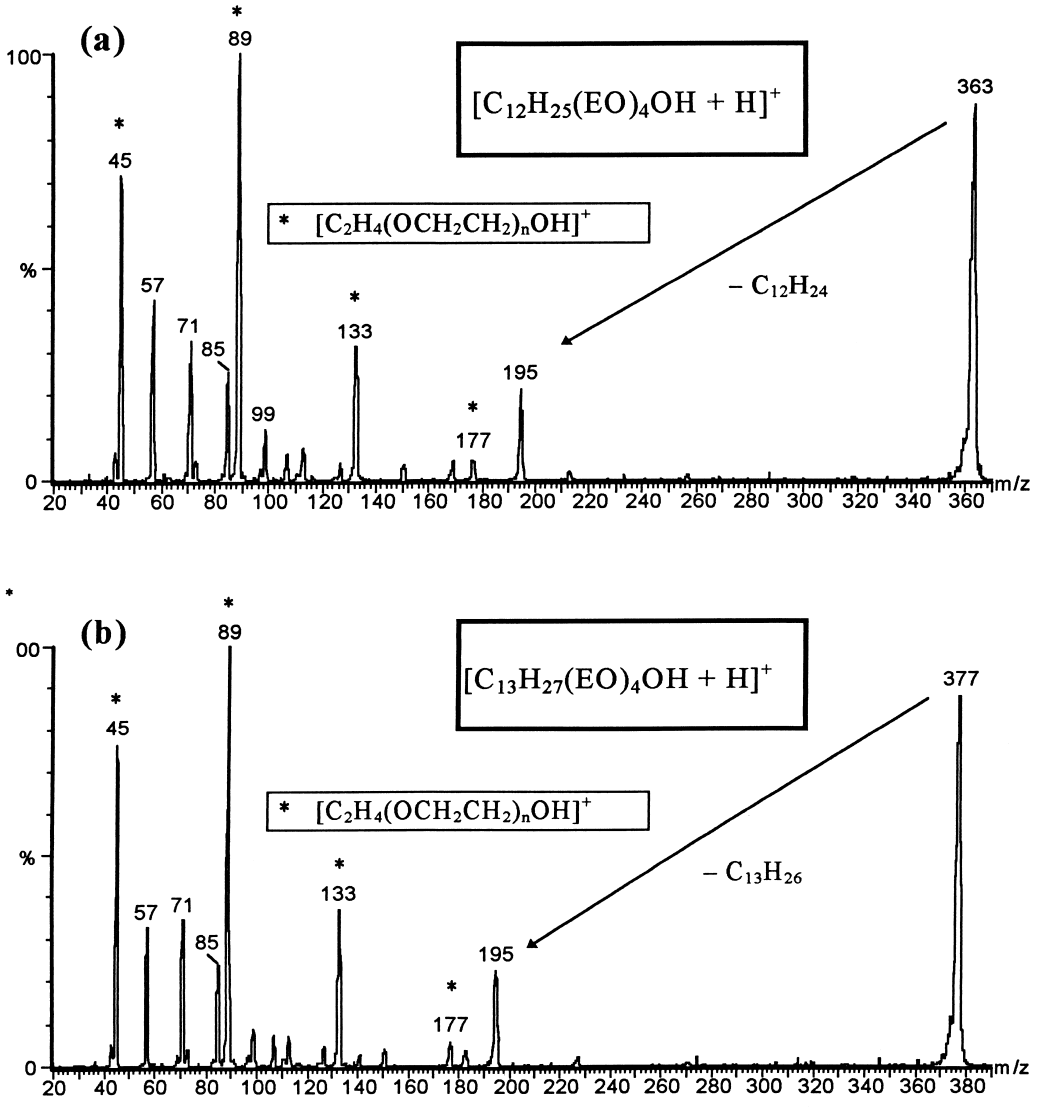

Figure 5. APCI(+) MS/MS spectra of the *m/z* 363 **(a)** and *m/z* 377 **(b)** ions in Dobanol 23PES04 (CID gas–argon, collision energy −40 eV, analyzer pressure -2.0×10^{-5} mbar).

the form $[R(OCH_2CH_2)_nOH + H]^+$. This ion series can be formed in two ways: from the protonation of alcohol ethoxylates, $[M_2 + H]^+$, and/or by desulfation and protonation of alkyl ethoxysulfates of the form $[M_1 - NaSO_3 + 2H]^+$. Because APCI is a "harder" ionization method than ESI, desulfation of alkyl ethoxysulfate is a distinct possibility in contrast to the observation of intact alkyl ethoxysulfates in the ESI(+) mode. Furthermore, the results presented above show that SO_3 is very easily lost from AES. Finally, we have shown that the unsulfated ethoxylate is at best only a minor component of the Dobanol 23PES04 surfactant mixture and there is no reason to believe that APCI(+) responds selectively to alcohol over sulfate (i.e., that the intact sulfate is present but completely unobserved).

Low energy CID spectra of two ions in this series ($[C_{12}H_{25}(EO)_4OH + H]^+$) and ($[C_{13}H_{27}(EO)_4OH + H]^+$) are presented in Figure 5. It is immediately obvious that the desulfated, protonated precursor ions generate more product ions under low energy CID conditions than the ions produced in the ESI(+) and ESI(−) modes. The ion at *m/z* 195, $[H(OCH_2CH_2)_4OH + H]^+$, which corresponds to the loss of the alkyl chain (as an alkene) from the precursor ion, provides a direct indication of the length of the alkyl chain by subtraction of its mass (*m/z* 195) from that of the precursor ion to get the mass of the alkene. In addition, the ions at *m/z* 45, 89, 133, and 177 (denoted by asterisks (*) in Figure 5) represent ether cleavages between the ethylene oxide units in the molecule. Ions in this series are of the form $[C_2H_4(OCH_2CH_2)_nOH]^+$. For precursor ions with low EO numbers ($n < 5$), a product ion in this series is obtained for every value of n in the precursor ion. However, we observed that when $n > 4$, product ions were not formed for the higher values of n. This phenomenon was also reported by Lattimer and co-

Table 2. Oligomeric distribution of alkyl ethoxysulfates in Dobanol 23PES04 by ESI(+) and APCI(+). Percent composition was derived from the relative mass spectral ion intensities of the C_{13} alkyl chains of individual oligomers in each series

EO number (n)	% Composition by ESI(+) $[M_1 + Na]^+$	% Composition[a] by APCI(+) $[M_1 - NaSO_3 + 2H]^+$
0	15.2	0.0
1	7.7	0.1
2	9.0	6.9
3	13.2	15.4
4	16.3	23.0
5	13.6	16.0
6	7.5	12.9
7	8.7	8.9
8	4.6	6.8
9	2.8	4.7
10	0.9	3.2
11	0.5	2.1 (n = 11–15)
n_{avg}	3.8	5.3

[a]APCI(+) was performed at low resolution, increasing the value of n_{avg}.

workers [10]. Nevertheless, APCI(+) does produce ions which under low energy CID conditions generate product ions which reveal information on the structural characteristics of the precursor ion.

Quantification

Table 2 indicates the percent composition of the individual AES species and the average EO oligomer number in the Dobanol 23PES04 sample based on the mass spectral ion intensities in the ESI(+) and APCI(+) modes. The average EO oligomer number was calculated from

$$n_{avg} = \frac{\sum_{i=j}^{k} n_i I_i}{I_{tot}} \quad (1)$$

where n_{avg} is the average oligomer number, j is the lowest observed oligomer number in the mass spectrum, k is the highest observed oligomer number in the mass spectrum, n_i is the ith oligomer, I_i is the mass spectral ion intensity of the ith oligomer, and I_{tot} is the total mass spectral ion intensity of all the oligomers from j to k. This, of course, assumes that sensitivity is the same for each oligomer. Hunt et al. [13] have shown on an instrument very similar to the one used in this study that cone voltage has a significant effect on the relative intensities of the various oligomer ions in ESI MS. We have noticed similar instrumental effects (see below). Ignoring all peaks but the lowest mass peak in each isotope cluster, as was done for the data in Table 2, shifts the distribution towards lower EO number. The contribution of the $n = 11$ oligomer compared to the $n = 0$ oligomer is approximately 78% of its correct value when calculated in this manner. This, however, does not have a large effect on the calculated average EO number because only the ions near $n = 4$ have a large influence on this calculation. If desired, the calculation can be carried out using all the ions in the isotope clusters, if there are no interferences for any of these ions.

There appears to be reasonable agreement between the two methods, indicative of the ability to approximate EO distribution (and alkyl distribution) in ESI(+) and APCI(+). However, more precise quantitative analyses cannot be achieved without calibration methods or internal standards (a quantitative method for the determination of AES using calibration curves has recently been developed [7]).

It should also be noted that the average EO number (data not shown) calculated from the ESI(−) mass spectral ion intensities ($n_{avg} = 1.0$) disagreed substantially with that obtained by ESI(+) and APCI(+), as well as with the number reported by the supplier ($n_{avg} = 4$). The reason for this large discrepancy is unclear to us and further investigation is required. Although the average EO numbers calculated from ESI(+) and APCI(+) are reasonably close to one another (and to that of the supplier), the absence of the lower oligomers in APCI(+) spectra is unexpected and may be related to specific losses of these species in the higher energy ionization process.

A more in-depth study revealed that the average EO number obtained was dependent on a number of instrumental/tuning factors [more so in the ESI(+) and APCI(+) modes than in the ESI(−) mode]. These factors included source temperature, cone voltage, resolution, and APCI probe temperature. Perhaps the most severe effect was that of resolution: operating at lower resolution enhances ions in the high mass region relative to those at low mass. This effect was not unique to AES surfactants; similar effects were observed with other oligomeric species such as PEG. Differences in the various ionization processes undoubtedly also contribute to the observed variations in the oligomer distribution.

In general, our results show that quantification of individual AES species, based on ESI and APCI mass spectral ion intensities, should be interpreted with caution in the absence of any other quantitative information.

Matrix Effects

Preliminary experiments were done using other anionic surfactants closely related to AES, in particular an alkyl sulfate mixture and an alkyl(propoxy/ethoxy)sulfate mixture in the APCI(+) and ESI(+) modes to study the effect of the presence of other species in solution (matrix effects). Early results indicate that APCI(+) is not strongly affected by matrix effects (i.e., the APCI(+) signal intensity for any given ion is independent of the concentration of additive in solution). On the other

hand, ESI(+) ion intensities decrease significantly as the concentration of ionic additives such as picolinic acid and sodium sulfate increases. Thus, for quantitative work, APCI appears to be more tolerant than ESI to the presence of other species in solution.

A likely explanation for this lies in the fact that APCI is a bulk technique in which all species in solution are ionized to the same degree of efficiency; therefore, the ions which reach the detector in APCI mode should be representative of the relative concentrations of the molecules in the bulk of solution. In other words, an increase in additive ions produced in APCI results in a subsequent increase in the total ion current which means that the mass spectral ion intensity of the analyte ion is conserved. The ESI mass spectrum can be considered a representation of the unpaired ions at the surface of a given drop. When no additive is present, only unpaired positive analyte ions are present at the drop surface. However, as the amount of additive increases, the analyte ions at the surface of a drop are replaced by additive ions. The decrease in the number of analyte ions at the drop surface causes a decrease in analyte ions available for mass spectrometric detection, resulting in analyte suppression effects. A more detailed discussion of matrix effects in ESI can be found elsewhere [14]. More in-depth experiments dedicated to the study of matrix effects will be required; we only wish here to report our initial observations.

Conclusions and Future Work

ESI(+), ESI(−), and APCI(+) all produce ions for individual AES components. The simplest spectra of commercial oligomer mixtures are provided by ESI(−) and APCI(+) and the data obtained from both ESI(+) and APCI(+) can be used to estimate the average EO number for the mixture. The ions produced in ESI do not provide much structural information when subjected to low energy CID, whereas those produced by APCI(+) do indicate the length of the alkyl chain and provide some information on the number of ethylene oxide groups in the molecule. In addition, APCI(+) is less susceptible than ESI to matrix effects, which is important when dealing with surfactants in complex matrices. Thus APCI(+) provides an additional and very useful tool for the analysis of anionic surfactants.

APCI(+) mass spectrometry also has been carried out on anionic surfactants similar to Dobanol 23PES04, including alkyl sulfates, alkyl propoxysulfates, and alkyl (propoxy/ethoxy) sulfates, which will be discussed in a future publication. In particular we are interested in using APCI(+) MS/MS for the direct determination of the EO/PO monomer sequence of surfactants containing both ethylene oxide and propylene oxide units in complex mixtures.

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